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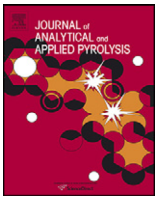

Fast pyrolysis of biomass thermally pretreated by torrefaction☆

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ABSTRACT

Torrefied biomass samples were produced from hardwood and switchgrass pellets using the biochar experimenter's kit (BEK) reactor and analyzed for their utility as pretreated feedstocks for biofuels production via fast pyrolysis. The energy efficiency for the BEK torrefaction process with propane gas as fuel source was about 50% for hardwood pellets and over 67% for switchgrass, but the energy retained in the torrefied product ranged between 72 and 92% of the initial biomass energy content resulting from a high product yield of 70–88 wt%. The liquid pyrolysate by-product of the torrefaction process was an aqueous solution of mainly acetic acid and levoglucosan associated with dehydration of the carbohydrate fraction of the raw biomass. Subsequent fast pyrolysis in a fluidized bed led to production of pyrolysis oil with lower acidity and increased energy content compared with pyrolysis of non-torrefied biomass. However, the yield, carbon conversion and energy conversion to these pyrolysis oils were decreased with the torrefection pretreatment which predisposed the biomass for conversion to biochar rather than liquid products.

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1. Introduction

Torrefaction is a low temperature thermal conversion that improves the fuel properties of biomass. Considered a mild form of pyrolysis, the slow heating of torrefaction occurs at atmospheric pressure and in the 200–300 °C temperature range in the absence of oxygen [1]. The torrefied product has reduced moisture content and increased energy density, retaining about 70% of initial mass and up to 90% of its initial energy. Torrefied biomass is also hydrophobic and easily ground, improving its potential for storage and transport [2].

When biomass is heated, drying occurs first. As the temperature is raised above 200 °C, significant quantities of hemicellulose decompose into volatiles and char products, while some devolatilization and carbonization of lignin and cellulose begin to occur [2]. Biomass browns and releases carbon dioxide, acetic acid, and additional moisture. Around 280 °C, carbon monoxide and hydrocarbons form, as well as phenols, cresols, and other heavier products [3]. It is above 300 °C that pyrolysis, severe decomposition of the substrate, begins. In addition to production of charcoal for industrial fuel, torrefaction is potentially useful as a pre-treatment for fast pyrolysis of biomass to pyrolysis oil (bio-oil) [4–8]. Any use of a fast pyrolysis feedstock with lower oxygen content, such as torrefied biomass, creates a less oxygenated bio-oil that may be more stable than that produced from conventional pyrolysis feedstocks, and could therefore be more easily stored, transported, and upgraded to consumer-quality vehicle fuel.

Torrefaction can be carried out in reactors intended for fast or slow pyrolysis processes typically used for bio-oil/biochar production. The fundamental challenge is the need for tight control of the reactions to prevent complete devolatilization especially within the unstable temperature window that is suited for torrefaction. Herein, we adopted the biochar experimenter's kit (BEK) reactor for this purpose. To our knowledge there has not been any reported use of the BEK for torrefaction purposes. We examine the properties of the torrefied products and the utility of torrefaction pre-treatment as feedstock for the production of pyrolysis oil in a bench-scale fluidized bed reactor in terms of product yield and quality.

2. Materials and methods

2.1. BEK reactor system

The biochar experimenters kit (BEK), an open source biochar reactor design, developed, manufactured and distributed by All Power Labs, LLC (APL) of California was used to carry out the torrefaction process. The layout of the system is presented in Fig. 1. The kit consists of two concentric cylindrical vessels with an open annulus where biomass is fed and heated. Heat source for direct and/or indirect heating of the biomass is provided by

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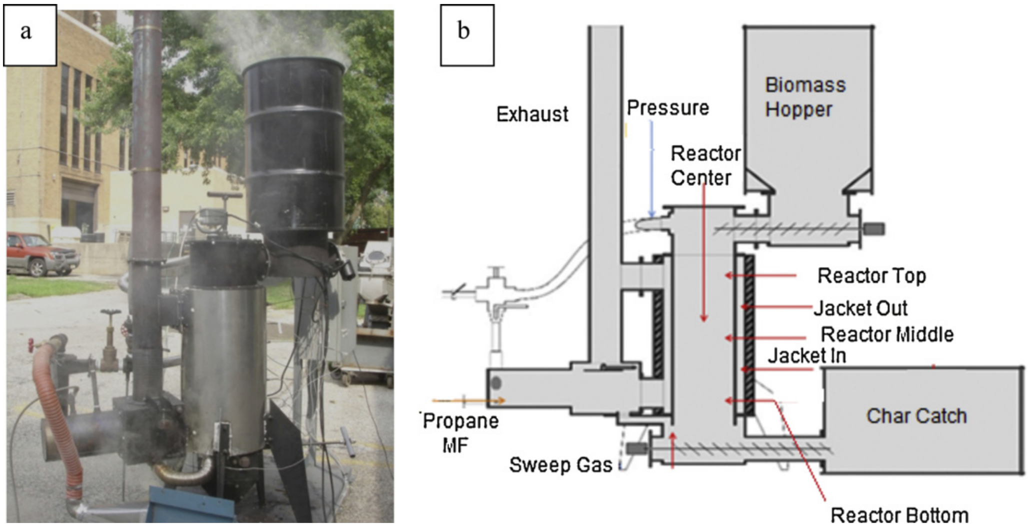

Fig. 1. The biochar experimenter's kit (BEK), (a) image and (b) layout and modified instrumentation. Red arrows indicate location of thermocouples.

hot gases generated from an air heater fueled by propane gas. The hot combustion gases are channeled through the external and internal annuli to provide indirect heating by conduction heat transfer through the walls and into the biomass. The design has a provision (through valve opening) that allows for some of the combustion gases to be channeled through the biomass to provide direct heating. Several changes were made to the original designs which are noteworthy. These include replacing the false bottom, plus addition of extensive instrumentation to accomplish appropriate control of the system and for pertinent data acquisition. A new igniter, a combustion air fan and a propane mass flow controller were installed to provide adequate combustion and control of the air heater flame, the primary heat source. The fan frequency and propane flow rates were calibrated to determine precise equivalent air–fuel ratios, excess oxygen and energy input into the system. For that purpose thermocouples were installed (Fig. 1) to trend the temperature profiles along the system. Even with this, no true energy balance could be established due to the excessive heat losses characteristic of the BEK. Nevertheless the focus of the experiment was on producing torrefied biomass as a pretreated pyrolysis feedstock. Liquid product was collected as condensate in a trap along the reactor exhaust line.

2.2. BEK instrumentation

A National Instruments cDAQ 9178 data acquisition system was used to collect input data from instruments which were sent to LabView software protocols. In all there were two thermocouple input modules, a ±10 V output module, a ±10 V input module, a ±20 mA output module, and a ±20 mA input module all of which were capable of expansion. A 0–1 psi differential pressure transducer, employed at 0–1 V output signal, was used to measure the freeboard pressure.

An Allicat Mass Flow Controller was used to control propane mass flow rate and to monitor the propane temperature. The controller accepts a 0–50 standard liter per minute (SLPM) input signal scaled to 0–5 V which outputs two 0–5 V signals scaled to 0–50 SLPM (actual flow) and 0–180 °C (propane temperature). The system was instrumented such that the controller exhibited a steady state error at all times; it, usually taking place at a propane flow rate of approximately 0.5 SLPM lower than the set point. A total of seven thermocouples were installed on the BEK. The thermocouples tips were located roughly as shown in Fig. 1.

2.3. Bench scale fast pyrolysis

Torrefied feedstocks were ground to a mean particle size of 2 mm in a Wiley Mill and dried in an oven to <10 wt% moisture prior to the pyrolysis experiments. Fast pyrolysis was carried out in a bubbling fluidized bed of quartz sand at temperatures of ~500 °C [9,10] at feed rates between 1.6 and 2.5 kg/h. The system comprised a 7.5 cm (3-in.) diameter fluidized bed reactor section, followed immediately by 2 cyclones to remove biochar. The pyrolysis vapors were condensed by a series of 4 condensers cooled by cold water (~4 °C) and the remaining aerosols were collected by electrostatic precipitators. Pyrolysis oil and biochar yields were determined gravimetrically and non-condensable gas was measured using a Metris gas flow meter. Product yields were then corrected to account for unrecovered products using a non-linear optimization protocol [11]. Pyrolysis experiments were performed in duplicate or triplicate and all results are averages of the set of experiments.

2.4. Feedstock and product characterization

Pyrolysis oil water content was determined by Karl–Fischer (K–F) titration using 3:1 methanol: chloroform as solvent and HYDRANAL Karl–Fischer Composite 5 (Fluka) as titrant. Calorific values of pyrolysis oil were determined using a Parr 1281 or Leco AC600 bomb calorimeter. Elemental analyses (C, H, N, S) of the feedstocks and products were determined using a Thermo Flash EA1112 CHNS/O analyzer, by complete combustion of the material followed by GC quantification of the combustion products. Oxygen was then determined by difference after accounting for CHNS ash and water. Ash was determined as the percentage remaining after heating a sample in a muffle furnace in air to 650 °C for 6 h. Total acid number (TAN) was measured by inflection point according to a method modified from ASTM D-66, using wet ethanol as the titration solvent.

Gas Chromatography with Mass Spectroscopy detection (GC/MS) analysis of pyrolysis oil was performed on an Shimadzu GC-2010 equipped with a mass selective detector (MSD). The column used was a DB-1701, 60 m × 0.25 mm, 0.25 μm film thickness. The oven temperature was programmed to hold at 45 °C for 4 min, ramp at 3 °C/min to 280 °C and hold at 280 °C for 20 min. The injector temperature was 250 °C, and the injector split ratio set to 30:1. The flow rate of the He carrier gas was 1 mL/min. The pyrolysis oil samples for GC analysis were prepared as 3 ± 1 wt% solutions in

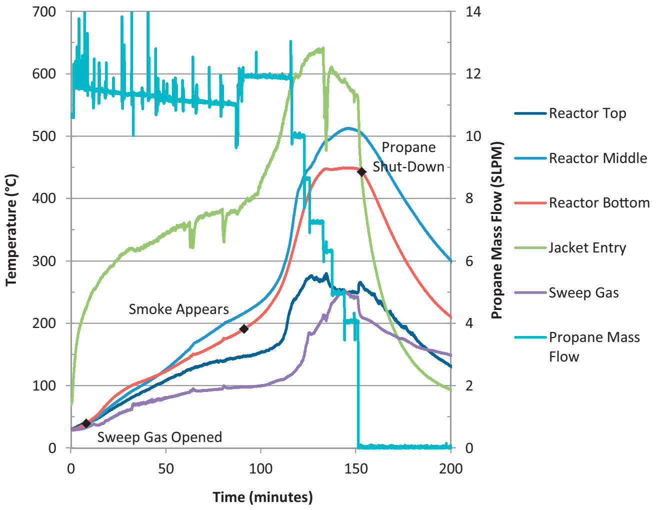

Fig. 2. Temperature profiles of BEK reactor system with sweep air through biomass.

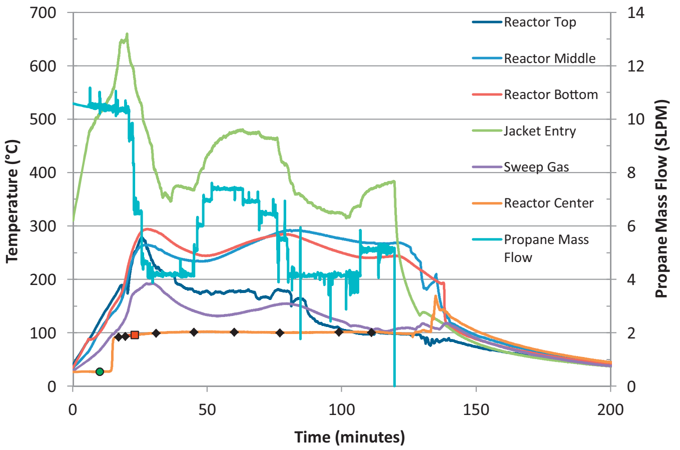

Fig. 3. Temperature profiles indicating manual control to achieve torrefaction conditions on the BEK. Wood pellets, 8/2/2011. Circle indicates point at which sweep gas was opened, square indicates point at which sweep gas was closed, and diamonds indicate points at which the reactor was mechanically stirred.

acetone which were filtered through a 0.45 μm PTFE filters prior to injection. Compounds were identified by comparison of their mass spectra with the NIST library. For quantification of individual pyrolysis oil compounds (those indicated in Table 7), response factors relative to the internal standard, fluroanthene were determined using authentic compounds [12,13].

The stability of the pyrolysis oil was evaluated by accelerated aging followed by average molecular weight determination using Gel Permeation Chromatography (GPC). Accelerated aging tests were modified from the protocol established by Oasmaa and Kuoppala [14]. This protocol ascertains that heating at 80 °C for 24 h is equivalent to one year storage at room temperature conditions. Herein, the pyrolysis oil was placed in a sealed vial and heated in an oven at 80 °C for 8 and 24 h followed by molecular weight characterization using Gel Permeation Chromatography (GPC). The GPC instrument used was a Polymer Laboratories GPC-50, equipped with two identical Oligo-Pore GPC columns (polystyrene-divinylbenzene copolymer, 300 mm × 7.5 mm) in series heated at 50 °C. Dimethylformamide (DMF) was used as the mobile phase carrier liquid which was delivered at a flow rate of 1 mL/min. Samples were well dissolved (∼1 mg/mL) in DMF and filtered through a PTFE filter prior to use. Peak detection was done by refractive index (RI). The GPC columns were calibrated using five polyethylene glycol standards in the MW range of 105–3900. Phenol was added as an additional standard to expand the lower end of the MW range to 94.

3. Results and discussion

3.1. *BEK runs*

Several BEK runs were carried out between July and August 2011. The initial runs were necessary to establish control of the system operation and to learn how to establish consistent propane flow so as to maintain a tight torrefaction temperature window. Most of the initial runs demonstrated that the sweep gas did not always provide an increased heating efficiency. Rather, it led to smoking and runaway temperatures primarily due to excess air in the sweep gas which tends to support combustion of torrefied solid. The sudden rise in temperature trending in Fig. 2 demonstrates the challenges faced in maintaining the desired temperature window with the sweep gas open. Hence for most of the latter runs where data were collected for further analysis, the sweep gas was not used. Fig. 3 shows the techniques and protocol followed in order to maintain the desired temperature window of 230–300 °C. This was achieved by a combination of actions including the opening of the sweep gas for a short period to accelerate the heating followed by continuous stirring and then flame control by adjusting the air/propane ratio. The three BEK run conditions analyzed (Table 1) were July 28th, August 2nd, and August 5th. Table 2 presents the product yield and energy use for these three runs from which torrefied feedstock was produced for bio-oil production. As shown, yields were biomass-dependent but in most cases retaining greater than 77 wt% of the initial mass. Energy balance over the reactor was difficult to establish due to excessive losses of both material and energy through the flue gas. Nonetheless, the energy recovery if calculated as torrefied biomass energy content divided by raw biomass energy content, was estimated as 83 and 72 wt% for the hardwoods runs on the July and August conditions respectively and 93% for switchgrass. It has been reported that biomass torrefaction can retain about 80 wt% of the initial mass and over 90% of the biomass initial energy [6]. However, the estimated external (sensible) energy use via propane gas was 18.78 MJ, 7.17 MJ and 6.49 MJ per kilogram of torrefied biomass produced, respectively. The excessive amount for the July 28 run was necessary to attain the desired conditions within the shorter period of time thereby probably resulting to ineffective control. When the torrefied biomass energy recovery is defined on the basis of total energy input into the BEK system i.e., when calculated as energy in the torrefied product divided by feedstock and propane energy input the percent energy recovery of the torrefied product was substantially lower. These estimates were respectively 47%, 57% and 68%.

The torrefied solid product collected from the BEK was divided into three samples for further analysis and second stage pyrolysis in a fluidized bed based on the level of conversion as established by color (Fig. 4): black (most conversion), dark brown (partial conversion), and light brown (least conversion). Light brown, which was partially charred was closer to the raw biomass in coloration, but was expanded and flaky, with no remaining outer coating. Dark brown char was of a deep coffee color and had a flaky texture like the light brown samples. Black char was compacted and crumbled easily into powder. The mass breakdown of these fractions was approximately 37% light brown, 25% dark brown and 38% black. Although the localized temperatures resulting in these delineations are unknown they are assumed and appear to be within the 230–300 °C range recorded.

Table 1
BEK runs.

Date	Feedstock	Temperature	Time
28 July 2011	Wood pellets, 10–20 mm × 5 mm	230 °C	0.5 h
02 August 2011	Wood pellets, 10–20 mm × 5 mm	300 °C	1.0 h
05 August 2011	Switchgrass pellets, 10–20 × 5 mm	250 °C	1.5 h

Table 2
Mass and energy balance for the BEK reactor.

Feedstock	Hardwood pellets				Switchgrass pellets	
Date	7/28/2011		8/2/2011		8/5/2011	
	Mass	Energy	Mass	Energy	Mass	Energy
Material in [kg, MJ]	13.61	258.27	13.59	257.89	11.86	184.24
Product solid [kg, MJ]	10.45	211.95	9.41	185.98	10.50	171.07
Product gas [kg]	3.16		4.18		1.36	
Product yield [wt%]	76.78		69.24		88.53	
Propane in [L, MJ]	2270.00	196.33	780.00	67.46	787.50	68.11
External energy use/raw-feed [MJ/kg]		14.43		4.96		5.74
External energy use/solid-product [MJ/kg]		18.78		7.17		6.49
Prod energy/Raw biomass energy [%]		82.06		72.11		92.85
Prod energy/Energy in (Biom. & Prop.) [%]		46.62		57.16		67.79

3.2. *Compositional analysis*

The major components of the torrefied biomass were carbon, oxygen, and hydrogen (Table 3). Torrefaction was found to increase the carbon and ash contents while decreasing the amount of hydrogen and oxygen. For hardwood pellets the O/C ratio reduced from 0.73 to 0.43 for the fully torrefied char (black coloration) and for switchgrass it reduced from 0.85 (raw feedstock) to 0.23 for the fully torrefied product. This constituted about 10–15 wt% reduction in oxygen for hardwood pellets and over 25 wt% oxygen reduction for switchgrass. H/C ratios reduced modestly over the selected color range. The reduction in oxygen and hydrogen is likely due to the loss of water and light oxygenates during torrefaction. The reduced O/C ratio improves the heating value of the product retaining 80–90% of the energy content of the biomass discounting the heat input in creating it. The lower oxygen content of the darkest switchgrass product indicated that the potential for more deoxygenated pyrolysis products to be produced from it.

3.3. *Liquid pyrolysate by-product analysis*

Qualitative analysis of the pyrolysate from the BEK torrefaction runs was necessary to ascertain the composition of the liquid products and its source or the portion of the biomass composition that might have devolatilized upon torrefaction. As Table 4 presents most of the pyrolysate was water indicating torrefaction as viable densification process via dehydration. Importantly however, the major components besides water were acetic acid, acetol and levoglucosan. Acetic acid, typically produced from deacylation of hemicelluloses was up to 10 wt% (∼65% db) for hardwood and about 4 wt% (∼37% db) for switchgrass, in the liquid sample collected. Bearing in mind that these are carboxylic acids and oxygenates that contribute to pyrolysis oil stability issues the results suggest that torrefaction is potentially a viable pretreatment route for pyrolysis of biomass to fuel intermediates. Further elucidation of this would be expounded by carrying out fluidized bed fast pyrolysis on the torrefied samples. Levoglucosan a dehydration product of glucose and cellulose [15], was 15% db for wood and about 63% db for switchgrass. This demonstrates that potential sugar content is lost in the torrefaction process, suggesting that torrefaction may be a poor pretreatment for biofuel production via biochemical methods where sugar must be maximized. Table 4 also shows that only traces of lignin derived compounds were eluted at the torrefaction temperatures we encountered. It appears therefore that the majority of the liquid pyrolysate from the torrefaction process came from the carbohydrate portion of the biomass, as proposed by others [16].

3.4. *Bench scale fluidized bed fast pyrolysis of torrefied biomass*

Fast pyrolysis experiments were performed on the torrefied feedstocks using the USDA's Agricultural Service's (ARS) bench scale fluidized bed reactor [9,10]. In the case of hardwood pellets pyrolysis experiments were conducted on non-pretreated/torrefied material, bulk torrefied product from the BEK (produced 02 August 2011) and by physical selection of just the darkest torrefied pellets from the same BEK torrefaction process. For switchgrass only the non-pretreated/torrefied pellets and bulk BEK torrefied products were further pyrolyzed. Table 5 compares the yields of pyrolysis oil, biochar and non-condensable gases from

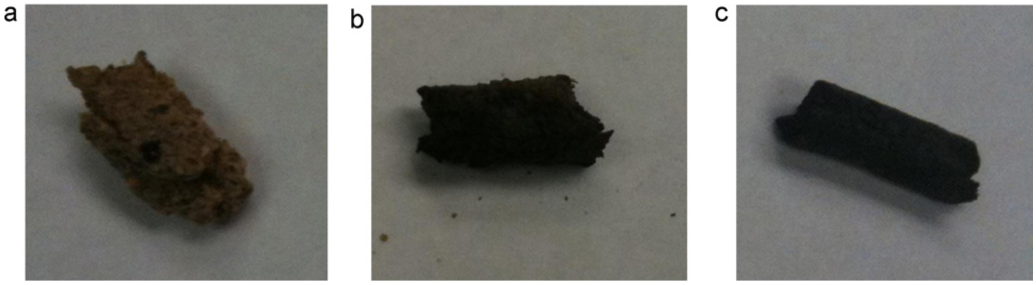

Fig. 4. Torrefied biomass samples (a: light brown, b: dark brown, c: black).

Table 3
Elemental analysis of torrefaction products.

	Raw	Light	Dark	Black
Hardwood 28-July				
C	47.07	49.42	50.36	58.86
H	6.03	5.93	5.78	5.08
N	0.43	0.15	0.13	0.18
S	0.00	0.00	0.00	0.00
O	45.84	43.88	43.04	34.80
Ash	0.63	0.62	0.69	1.08
O/C	0.73	0.67	0.64	0.46
H/C	1.55	1.43	1.37	1.04
HHV [MJ/kg][a]	19.1	19.7	19.9	21.8
HHV [MJ/kg, DAF]	19.2	19.8	19.9	22.0
Hardwood 2-August				
C	47.07	45.68	50.97	59.86
H	6.03	5.50	5.72	4.93
N	0.43	0.14	0.14	0.19
S	0.00	0.00	0.00	0.00
O	45.84	48.11	42.44	31.93
Ash	0.63	0.57	0.73	3.09
O/C	0.73	0.79	0.62	0.40
H/C	1.54	1.44	1.35	0.99
HHV [MJ/kg][a]	19.1	18.4	20.0	21.9
HHV [MJ/kg, DAF]	19.2	18.5	20.1	22.6
Switchgrass 5-August				
C	40.36	42.53	44.40	55.98
H	5.68	5.65	5.78	4.30
N	1.10	1.06	1.38	1.90
S	0.00	0.05	0.09	0.09
O	45.54	42.99	40.40	19.96
Ash	7.33	7.73	7.96	17.77
O/C	0.85	0.76	0.68	0.23
H/C	1.69	1.59	1.56	0.92
HHV [MJ/kg][a]	16.8	17.3	17.9	19.9
HHV [MJ/kg, DAF]	18.1	18.8	19.5	24.2

[a] Calculated according to [17].

Table 4
Concentration of compounds in Aqueous Phase Torrefaction Pyrolysate (GC/MS).

Compound (wt%)	Wood chips	Switchgrass
Water	64.4	75.95
Acetic acid	10.04	3.88
Acetol	2.7	0.025
Furfural	0.06	0.07
Phenol	0.06	0.03
Guaiacol	0.08	0.025
o-Cresol	0.03	0.03
p-Cresol	0.03	0.025
m-Cresol	0.04	0.025
Methyl guaiacol	0.05	0.06
Syringol	0.14	0.55
Levoglucosan	2.38	6.72

Table 5
Fast pyrolysis product yields (wt%) for torrefied and non-torrefied hardwood and switchgrass pellets.

	Hardwood pellets			Switchgrass pellets	
Pretreatment	None	BEK bulk	BEK black	None	BEK bulk
Total pyrolysis liquid	71.1	52.6	16.5	57.1	50.6
Char	10.3	15.7	60.0	19.9	35.3
Non-condensable gases	19.7	33.1	26.1	24.3	29.3

torrefied and non-torrefied (raw) hardwood and switchgrass pellets. As the degree of torrefaction increased, the absolute mass yield of pyrolysis oil decreased and the yield of biochar and non-condensable gases increased. However, the pyrolysis oil proved to contain less oxygen, had lower acidity and higher energy content as the degree of torrefaction increased. As shown in Table 6 pyrolysis oils derived from raw wood, had an O/C ratio of 0.53 and a dry basis energy content of 23.8 MJ/kg. Those produced from torrefied wood pellets had an O/C ratio of 0.50 for the liquids from the bulk pretreated/torrefied material and 0.26 for the products of the darkest pellets and energy contents of 24.1 and 27.7 MJ/kg, respectively. For switchgrass the changes in the composition of the pyrolysis oil with torrefaction pretreatment were more subtle. The O/C ratio of the pyrolysis oil increased from 0.40 to 0.48 with torrefaction 0.18 and the energy content increased from 24.0 to 26.2 MJ/kg. Quantitative GC/MS analysis (Table 7) reveals that for both feedstocks the amount of acetic acid in the pyrolysis oil decreased with extent of torrefaction. The decrease in acetic acid was more dramatic for the wood pellets than for the switchgrass, consistent with the observation that the liquid pyrolysate from the torrefaction of the switchgrass pellets had a lower concentration of acetic acid (Table 4) than it did from the wood pellets. Furthermore, acetol concentration in the pyrolysis oil decreased with the level of torrefaction pretreatment and the concentration of non-methoxylated phenols (phenol, cresols) increased. Despite being found in the liquid by-product of the torrefaction pretreatment process, levoglucosan did not decrease in concentration in the pyrolysis oil. Another measure of acidity, total acid number (TAN) also indicated that the effect of the torrefaction pretreatment on the acidity of the pyrolysis oil was greater for wood pellets than for switchgrass. TAN reduced from 135 mg KOH/g for pyrolysis oil from raw wood pellets to 73 mg KOH/g for the bulk torrefied material to 56 mg KOH/g for the separated black pellets. For switchgrass pyrolysis oils the TAN was reduced from 117 to 83 mg KOH/g with the thermal pretreatment of the pellets.

The reduction in the acidity and concentration of oxygenated compounds that are major contributors to the instability of pyrolysis oils suggest that pyrolysis oils produced from biomass pretreated by torrefaction should be more stable than those produced from raw biomass. Therefore we compared the stability of the pyrolysis oils using an accelerated aging protocol by heating the samples at 80 °C for periods of 8 and 24 h and monitoring the changes in average molecular weight by GPC. Fig. 5 shows the changes in the weight average molecular weight (Mw) of the pyrolysis oil over this accelerated aging period. For the products derived from wood pellets, the average size of the molecules in the pyrolysis

Table 6
Characterization of fast pyrolysis oils produced from biomass pretreated by torrefaction (dry basis values in parenthesis).

	Hardwood pellets			Switchgrass pellet	
Pretreatment	None	BEK bulk	BEK black	None	BEK bulk
Water (wt%)	9.4	18.7	4.1	19.1	16.5
C (wt%)	49.5 (54.6)	47.1 (57.4)	66.0 (68.8)	46.1 (56.7)	50.9 (59.7)
H (wt%)	5.4 (6.0)	4.6 (5.5)	5.8 (6.0)	4.8 (5.8)	4.9 (5.6)
N (wt%)	0.2 (0.2)	0.2 (0.3)	0.3 (0.3)	1.8 (2.2)	2.3 (2.6)
O (wt%)	35.6 (39.2)	30.9 (39.3)	23.4 (24.3)	28.2 (35.2)	27.0 (32.0)
O/C (mol)	0.53	0.50	0.26	0.48	0.40
H/C (mol)	1.3	1.1	1.0	1.2	1.1
HHV (MJ/kg)	21.5 (23.8)	22.7 (24.1)	26.6 (27.7)	19.4 (24.0)	22.8 (26.2)
TAN (mg KOH/g)	135	73	56	117	85

Table 7
Quantification of pertinent compounds in fast pyrolysis oils produced from biomass pretreated by torrefaction (dry basis values in parenthesis).

	Hardwood pellets			Switchgrass pellet	
Pretreatment	None	BEK bulk	BEK black	None	BEK bulk
Acetic acid	9.3 (10.2)	7.7 (9.2)	4.1 (4.3)	6.9 (8.5)	4.6 (5.5)
Acetol	9.5 (11.0)	5.8 (7.0)	1.3 (1.4)	12.4 (15.3)	5.8 (6.9)
Furfural	0.2 (0.2)	0.2 (0.2)	0.2 (0.2)	0.1 (0.1)	0.1 (0.1)
Phenol	0.2 (0.2)	0.2 (0.2)	1.7 (1.8)	0.2 (0.2)	0.1 (0.1)
Guaiacol	0.1 (0.1)	0.1 (0.1)	0.1 (0.1)	Trace	0.1 (0.1)
o-Cresol	0.2 (0.2)	0.1 (0.1)	0.8 (0.9)	0.1 (0.1)	0.1 (0.1)
p-Cresol	0.1 (0.1)	0.1 (0.1)	0.8 (0.9)	0.1 (0.1)	0.1 (0.1)
m-Cresol	0.1 (0.1)	0.1 (0.1)	1.0 (1.1)	0.1 (0.1)	0.1 (0.1)
Levogulcosan	9.2 (10.7)	11.0 (13.2)	9.6 (10.1)	4.8 (6.0)	5.6 (6.7)

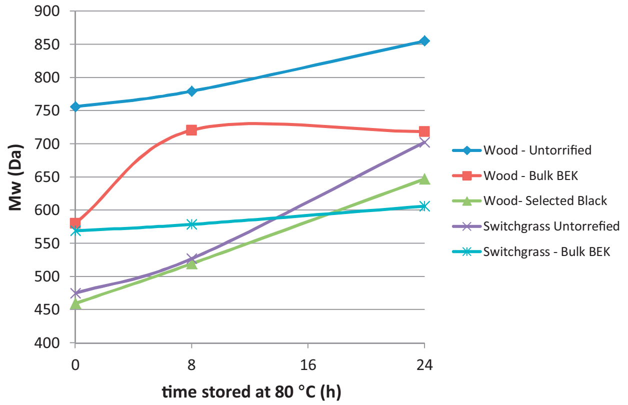

Fig. 5. Changes in weight average molecular weight (Mw) for fast pyrolysis oils with storage at 80 °C.

oil decreases with the degree of torrefaction pretreatment as shown by the starting Mw for each of the samples. This trend does not hold for the pyrolysis oils from the switchgrass pellets with torrefaction resulting in fast pyrolysis oils with a higher average Mw than those from the raw pellets. The aging tests show that the pyrolysis oils from both raw biomasses exhibit instability as shown by the nearly linear increase in Mw with accelerated storage. For the pyrolysis oils produced from biomass with torrefaction pretreatment the storage behavior is different. The pyrolysis oils produced from the wood pellets bulk BEK torrefaction product exhibited a Mw increase over the first 8 h of storage but then the Mw remained nearly steady over the remainder of the storage period. The pyrolysis oil produced from the selected black torrefied wood pellets exhibited a constant increase over the storage period. However, it is worth noting that while the Mw increased during storage for the pyrolysis oils even with torrefaction pretreatment, the Mw for each was still lower at the end of the storage period compared to the pyrolysis oil from the raw biomass. For switchgrass pellets, the torrefaction resulted in a much more stable fast pyrolysis oil, with only a slight Mw increase over the storage period. Therefore although the pyrolysis oil from the torrefied material had a larger Mw initially, after the storage period the average size of the molecules was smaller in the pyrolysis oil from the torrefied biomass. Overall, torrefaction pretreatment had a positive effect on the storage stability of the pyrolysis oils.

As stated above the major difference between fast pyrolysis of the untreated biomass pellets and the torrefied biomass pellets was the larger yield of biochar produced from the torrefied samples. Table 8 shows that, on an elemental basis, there is little difference between the fast pyrolysis biochars of raw biomass pellets and those produced from the bulk products of the BEK. For the wood pellets the O/C ratio was found in the range of 0.03/1 and an H/C ratio of 0.4–0.5/1 for the hardwood feedstocks. For the switchgrass the O/C ratios were around 0.18:1 and H/C ratios about 0.6/1. The heat of combustion of the biochars produced from the hardwood pellets was around 25 MJ/kg (~30 MJ/kg DAF), while that of switchgrass was 15–17 MJ/kg (~25 MJ/kg DAF); lower than the biochar from the wood pellets due to its higher ash and oxygen content. In the case of the manually selected most torrefied hardwood pellets the oxygen content increased (O/C = 0.11/1) and the energy content decreased to and 24.9 MJ/kg (27.4 MJ/kg DAF), suggesting that in the case of the highest degrees of torrefaction, the pretreatment predisposes both carbon and oxygen content to remain as solids during pyrolysis.

We present the carbon conversion from feedstock to fast pyrolysis products in Table 9. The carbon conversion was calculated for both a two step process ((i) torrefaction and (ii) fast pyrolysis) and the second step fast pyrolysis stage only (considering torrefied biomass as the starting material). The data from both feedstocks, torrefied and untorrefied, indicates that the percentage of the carbon that ultimately winds up in the pyrolysis oil decreases with the torrefaction pretreatment. This is concurrent with an increase in carbon that is converted to biochar. It shows that the torrefaction process predisposes the biomass to be converted to char during the torrefaction process. Owing to hydrogen loss through formation of water in dehydration reactions occurring during the torrefaction pretreatment step it there is a decrease of available hydrogen in the biomass to support the formation of liquid range organic molecules (see Table 3). Carbon converted via fast pyrolysis to permanent gases does not follow a trend for the hardwood pellets but does show the expected decrease with torrefaction for switchgrass, as easily decarboxylated and decarbonlyated groups are released in the torrefaction step. The lower carbon conversion values for the two step process (torrefaction followed by fast pyrolysis) are a reflection of the carbon lost to volatiles released in the initial torrefaction process.

In Table 10 we present the percentage of the biomass' energy recovered in each of the fast pyrolysis products again based on both the two-step (torrefaction and fast pyrolysis) processes and also only considering the second step, fast pyrolysis. For fast pyrolysis of the non-pretreated hardwood pellets, the pyrolysis oils contained 80% of the energy of the biomass pellets, the char 13% and the NCG 11%. For fast pyrolysis of the bulk torrefied material produced

Table 8
Analysis of fast pyrolysis biochar from torrefied feedstocks, dry basis (dry ash free values in parenthesis).

	Hardwood pellets			Switchgrass pellets	
Pretreatment	None	BEK bulk	BEK black	None	BEK bulk
Ash (wt%)	16.2	13.2	9.3	38.9	31.1
C (wt%)	77.0 (92.0)	79.7 (91.9)	76.2 (84.0)	46.6 (76.2)	52.3 (75.9)
H (wt%)	2.9 (3.5)	2.9 (3.4)	2.8 (3.1)	2.3 (3.8)	2.5 (3.7)
N (wt%)	0.3 (0.4)	0.3 (0.4)	0.2 (0.3)	1.8 (2.5)	1.6 (2.2)
O (wt%)	3.5 (4.2)	3.8 (4.3)	11.5 (12.6)	11.0 (18.2)	12.3 (17.9)
O/C (mol)	0.03	0.04	0.11	0.18	0.18
H/C (mol)	0.5	0.4	0.4	0.6	0.6
HHV (MJ/kg)	25.0 (29.8)	25.8 (29.8)	24.9 (27.4)	15.2 (24.9)	17.3 (24.7)

Table 9
Carbon conversion to fast pyrolysis products (%).

Pretreatment	Harwood pellets					Switchgrass pellets		
	None[a] FP only	BEK bulk[b] FP only	BEK bulk[a] 2 stage	BEK black[b] FP only	BEK black[a] 2 stage	None[a] FP only	BEK bulk[b]FP only	BEK black[a] 2 stage
Pyrolysis oil	67.0	49.4	40.7	10.3	10.1	58.3	45.0	40.0
Char	16.7	24.8	20.9	77.7	76.1	21.0	41.6	34.2
Non-condensable gases	16.4	25.8	21.3	12.0	11.7	20.7	13.3	10.9

FP, fast pyrolysis.

[a] Calculated using raw biomass as starting material.

[b] Calculated using torrefied biomass as starting material, produced from indicated BEK torrefaction.

Table 10
Biomass energy recovery in fast pyrolysis products (%).

Pretreatment	Harwood pellets					Switchgrass pellets		
	None[a] FP only	BEK bulk[b] FP only	BEK bulk[a] 2 stage	BEK black[b] FP only	BEK black[a] 2 stage	None FP only[a]	BEK bulk FP only[b]	BEK black[a] 2 stage
Pyrolysis oil	80.0	58.5	47.3	20.1	17.4	65.9	64.4	52.3
Char	13.1	20.0	16.0	68.0	59.3	18.0	34.1	27.9
Non-condensable gases	11.0	16.3	13.3	15.1	13.2	9.1	11.1	9.2

FP, fast pyrolysis.

[a] Calculated using raw biomass as starting material.

[b] Calculated using torrefied biomass as starting material, produced from indicated BEK torrefaction.

from the BEK, the pyrolysis oil contained 59% of the energy in the torrefied feedstock or 47% of the energy in the raw biomass. The distribution of energy content to the biochar from the bulk BEK product increased over that from the raw pellets, at 16% from the pyrolysis stage and 13% over the two stages. The energy distribution to the gas fraction of the pyrolysis products was also increased. The difference in the overall energy recovery when considering the two-stage processes compared with only the second stage reflects the energy lost as condensable and non-condensable volatiles released during the torrefaction process. Considering the manually separated darkest pellets, the energy distribution to biochar was greatly increased due to its high yield, with the biochar retaining 68% of the energy in the torrefied material and 59% of the energy in the biomass (this calculation assumes that 77% yield of this material is possible given the proper conditions, the energy yield for each product will be lower if the torrefaction yield is lower). For the switchgrass pellets the energy distribution followed the same trend as was observed for the wood pellets, but with less magnitude of difference between the energy distributions to pyrolysis oils for raw and torrefied starting materials. When considering the second stage, fast pyrolysis process only, 64% of the energy in the bulk BEK products was recovered in the pyrolysis oil, compared with a 66% energy recovery in the pyrolysis oil for non-torrefied switchgrass pellets. When considering the two stage process for the switchgrass pellets, 52% of the biomass energy content was recovered in the pyrolysis oil. However, as it was for the hardwood pellets, the distribution of the biomass energy into biochar was greatly increased by pretreatment with torrefaction. In fast pyrolysis of non-torrefied switchgrass pellets 18% of the energy is recovered in biochar, but 28% of the switchgrass' energy is recovered in biochar over the two stages, torrefaction and fast pyrolysis.

4. Conclusions

The biochar experimenter's kit (BEK) reactor fueled by propane gas was successfully used for torrefaction of hardwood and switchgrass pellets at the temperature range of 230–300 °C. The product yield was greater than 70 wt% while retaining over 80% of the initial biomass inherent energy. The process energy efficiency, however, was 46–57% for hardwood and about 68% for switchgrass with the latter consuming less external energy. Elemental analysis of the torrefied solid product shows significant oxygen reduction, the result of the release of oxygenates, including acids (mostly acetic acid), water and carbon oxide gases. Hydrogen content was also decreased as a result of dehydration reactions producing water. The torrefaction pretreatment lead to production of pyrolysis oils which were less acidic, more stable and of higher energy content than pyrolysis oils produced via a one stage fast pyrolysis process. However, the yields of these pyrolysis oils decreased with the extent of the torrefaction, while the yield of solid biochar increased. Also, recovery of biomass carbon and energy in the liquid fraction of the fast pyrolysis products decreased with the pretreatment; more of the carbon and hence potential energy was converted to the solid biochar product.

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